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RESEARCH ARTICLE

Dilution sampling and analysis of particulate matter in biomass-derived syngas

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Abstract Thermochemical biomass gasification, followed by conversion of the produced syngas to fuels and electrical power, is a promising energy alternative. Real-world characterization of particulate matter (PM) and other contaminants in the syngas is important to minimize damage and ensure efficient operation of the engines it powers and the fuels created from it. A dilution sampling system is demonstrated to quantify PM in syngas generated from two gasification plants utilizing different biomass feedstocks: a BioMax®15 Biopower System that uses raw and torrefied woodchips as feedstocks, and an integrated biorefinery (IBR) that uses rice hulls and woodchips as feedstocks. $PM_{2.5}$ mass concentrations in syngas from the IBR downstream of the purification system were 12.8–13.7 $\mu g \cdot m^{-3}$, which were significantly lower than the maximum level for catalyst protection (500 $\mu g \cdot m^{-3}$) and were 2–3 orders of magnitude lower than those in BioMax®15 syngas (2247–4835 $\mu g \cdot m^{-3}$). Ultrafine particle number concentration and $PM_{2.5}$ chemical constituents were also much lower in the IBR syngas than in the BioMax®15. The dilution sampling system enabled reliable measurements over a wide range of concentrations: the use of high sensitivity instruments allowed measurement at very low concentrations (~1 $\mu g \cdot m^{-3}$), while the flexibility of dilution minimized sampling problems that are commonly encountered due to high levels of tars in raw syngas (~1 $g \cdot m^{-3}$).

Keywords dilution source sampling, syngas characterization, biomass gasification, ultrafine particles

1 Introduction

Biomass, biologic materials from living or recently living organisms, is the oldest energy source known to mankind and is the modern world's fourth largest energy source following coal, petroleum, and natural gas [1]. Biomass for biofuels, biopower, and bioproducts as a substitute for fossil fuels has the potential to reduce greenhouse gas (GHG) emissions because the carbon dioxide (CO_2) released during biofuel combustion is compensated for by CO_2 uptake during plant growth. US Department of Energy (DOE) [2] established goals to supply 5% of power, 20% of transportation fuels, and 25% of chemicals from biomass in the US by 2030, approximately equivalent to 30% of the current petroleum consumption.

China has a biomass potential of 3511 million tons of coal equivalents (Mtce) as of 2004, of which 460 Mtce (13%) was exploitable [3]. China produces > 600 million tons (Mt) of crop residues each year, of which ~37% are used for cooking or heating and 38% are used for livestock forage. The remaining ~20% (> 100 Mt) are burned directly in the field [4,5]. Stoves for cooking and heating typically have low energy efficiency and degrade indoor air quality, resulting in adverse health effects [6,7]. Developing cleaner and more efficient biomass conversion technologies, especially those using non-food biomass feedstocks, will improve people's living standards, reduce CO_2 and pollutants emissions, and support rural economic development [8].

The most promising route to create a biobased industry is to develop integrated biorefineries (IBR) capable of efficiently converting a broad range of biomass feedstocks into biofuels, biopower, and other bioproducts [9]. Biorefineries typically use a "sugar platform" based on biochemical conversion or a "syngas platform" based on thermochemical conversion. An effective thermochemical processes involves gasification of biomass to produce

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syngas followed by either electricity production through combustion or conversion of the purified syngas to fuels and chemicals [10]. A critical step in this process is the cleaning of syngas. Besides the major useful gaseous constituents (i.e., carbon monoxide (CO) and hydrogen (H_2)), syngas produced by biomass gasification contains various amount of CO_2, methane (CH_4), organic gases (e.g., benzene, toluene, and xylenes (BTX)), inorganic gases (e.g., ammonia (NH_3), hydrogen sulfide (H_2S), and hydrogen chloride (HCl)), tars, char, and ash [11,12]. Technologies for removing or reducing impurities such as sulfur- (S) or nitrogen- (N) containing compounds from syngas are commercially available; however, methods for characterization and removal of tars (high molecular weight hydrocarbons) and particles in syngas are still under development [13].

Particulates in the form of condensed tars [14], char, and ash adversely affect processes that utilize syngas. They may deposit on valves, fittings, pipes, heat exchangers, particle filters, and catalytic reactors, thereby causing fouling and reducing system efficiency. They may clog fuel lines and injectors in internal combustion engines. Tars with S or N hetero atoms (e.g., thiophene and pyridine) can also poison catalysts used to convert syngas to fuels. For example, the iron- or cobalt-based catalyst used in Fischer-Tropsch processes for converting syngas to diesel can be poisoned by part per billion by volume (ppbV) levels of tars with S or N atoms [13,15,16]. Therefore, it is important to measure the composition of particles at low concentrations in syngas.

The European Committee for Standardization (CEN) is developing a standard protocol for sampling and measurement of tar and particles in syngas from biomass gasification [11]. Similar to US Environmental Protection Agency (EPA) Method 5 for particulate matter (PM) emission testing from stationary sources [17], the CEN method consists of a heated probe, heated particle filter, condenser, a series of impingers containing a solvent for tar absorption, and equipment for flow and pressure control. The solid particle mass is measured by gravimetry after the filter sample is Soxhlet extracted to remove tar, and tar concentration can be determined either by gravimetry through solvent evaporation and weight differential, or by gas chromatography with mass spectrometry (GC-MS) or flame ionization detection (GC-FID). Since not all tar constituents (e.g., thermal labile or highly polar compounds) are amenable to GC analysis, this method may underestimate tar concentration. The accuracy of gravimetric analysis is affected by absorption or reaction of gases in the impingers [18]. This method is costly, time consuming, and cumbersome. Due to high uncertainties in the analysis, this method focuses on high tar and particle concentrations (in the range of $1\,\mathrm{mg\cdot m^{-3}}$–$300\,\mathrm{g\cdot m^{-3}}$).

Reported here is the application of a dilution sampling method to quantify PM concentrations and chemical composition in biomass-derived syngas. Dilution sampling methods are used for mobile sources and are also being applied to obtain real-world emissions from stationary sources [19–26]. These methods are readily adaptable to measure PM in syngas. It is recognized that dilution leads to partial pressure and temperature changes that affect the partition between gas and PM phases. However, syngas constituents are preserved when diluted by a clean and inert gas (e.g., nitrogen (N_2)) and the total quantity of condensable gases and primary particles can be collected and characterized along with the carrier gas composition. This approach was applied to two biomass gasification systems: 1) a BioMax®15 Biopower System located at the University of Nevada-Reno, and 2) a Pacific Renewable Fuels and Chemicals (PRFC) integrated biorefinery (IBR) plant located in Toledo, Ohio.

2 Experimental approach

2.1 Gasification systems

The BioMax®15 combines the biomass gasifier with an engine and generator to convert biomass to electricity and heat for combined heat and power applications (Community Power Corporation, Littleton, CO, USA) [27]. Granulated, pelletized, or chipped feedstocks are fed into an open top stratified downdraft type gasifier, where the feedstocks pass through several pyrolysis and reaction zones to generate syngas. The syngas passes through a reverse flow knockout pot to collect large char particles, a heat exchanger to preheat woodchips, and a fabric filter to collect particles. It is then sent to a 6-cylinder internal combustion engine coupled with an electric generator. The rated electrical power output for this system is 15 kW. BioMax®15 syngas was sampled during September, 2010. Three samples were taken with raw woodchip feedstock, and one sample was taken with a 50%/50% (weight) mixture of raw and torrefied woodchip feedstock. Syngas was sampled from a pipe between the filter and engine compartment where suction of the engine manifold caused a vacuum of ~2.5 kPa. As shown in Fig. 1(a), an ejector pump (Model HAVR 038HSS, Air-Vac Engineering, Seymour, CT, USA) driven by compressed N_2 was used to overcome the vacuum. The sampling line was heated to 60°C to minimize condensation.

The PRFC IBR pilot plant thermochemically transforms lignocellulosic biomass feedstocks into liquid transportation fuels. Syngas is produced by a proprietary pyrolysis/steam reforming process and is cleaned by a gas purification system, which includes a cyclone, filter, and wet scrubber to remove particles. The IBR processes 10–15 dry $\mathrm{tons\cdot day^{-1}}$ (dtpd) of biomass feedstock. The experiment was conducted in December, 2009, using rice hulls and woodchips (size-classified in the 0.3–6 cm diameter range) as feedstocks. Three valid samples were drawn from a location downstream of the syngas polisher

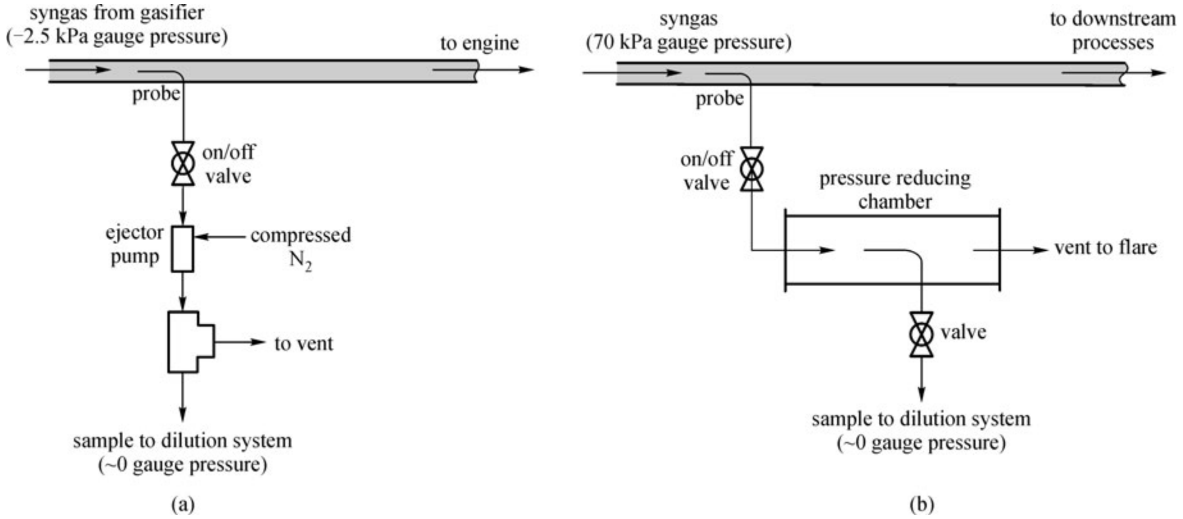


Fig. 1 Syngas sampling setup for: (a) an under-pressure system (–2.5 kPa) of the BioMax®15 gasification system, and (b) a pressurized system (70 kPa) in the PRFC IBR plant

and one sample from upstream. The syngas was produced at a gauge pressure of ~70 kPa, which was too high to be measured directly by the dilution sampling system. Therefore, a pressure reducing chamber, as shown in Fig. 1(b), was used to reduce pressure to ambient before entering the dilution sampler.

2.2 Dilution sampling

A portable dilution sampling system [28] was adapted for syngas characterization as shown in Fig. 2. The system is packaged into five modules: sample conditioning, gas, filter, real-time PM, and battery. The syngas sample first mixed with N_2 dilution gas in a turbulence-enhanced mixer, and aged for ~3 s in the residence chamber to equilibrate gases and particles. The diluted mixture passed through a cyclone to remove larger debris particles ($>$~7.6 μm) and then was collected or measured by various instruments.

The gas module includes: 1) real-time measurement of multiple gases including CO_2 in undiluted and diluted samples (to calculate dilution ratios), total volatile organic compounds (VOCs; isobutylene equivalent), CO, nitrogen oxide (NO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and oxygen (O_2); and 2) integrated measurement of CH_4 and VOCs by canisters, semi-VOCs by Tenax cartridges, carbonyls by 2,4-dinitrophenylhydrazine (DNPH) cartridges, and H_2S by Dräger tubes.

In the filter module, an inline impactor removed particles with aerodynamic diameter $>$ 2.5 μm. Gases of interest and $PM_{2.5}$ were collected on three parallel multistage filter packs to accommodate different analyses [29]. Filter Pack 1 included a front Teflon-membrane filter to measure mass by gravimetry and elemental composition (i.e., from sodium to uranium) by X-ray fluorescence (XRF) [30], and a back citric acid-impregnated cellulose-fiber filter to measure NH_3 by automated colorimetry. Filter Pack 2 included a front quartz-fiber filter to measure inorganic ions (i.e., Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, and K^+) by ion chromatography (IC) [31], and a back potassium carbonate (K_2CO_3) impregnated cellulose-fiber filter to measure acidic gases (i.e., HCl, HNO_3, H_2SO_4, and SO_2) by IC. Filter Pack 3 included a front quartz-fiber filter to measure organic and elemental carbon (OC and EC, respectively) following IMPROVE_A thermal/optical protocol [32,33], and a back silver nitrate ($AgNO_3$)-impregnated cellulose-fiber to measure H_2S by XRF.

The real-time PM module consists of four instruments: 1) a micro-aethalometer (Model AE51, Magee Scientific, Berkeley, CA, USA) for black carbon (BC); 2) a condensation particle counter (CPC; Model 3007, TSI Inc., Shoreview, MN, USA) for particle number in the size range of ~0.01–2.5 μm (a dilution bridge was installed upstream of the CPC to adjust concentration to reduce coincidence errors); 3) an optical particle counter (OPC; Model 1.108, Grimm Aerosol Technik GmbH & Co., KG, Ainring, Germany) for size distribution in the range of 0.3–25 μm; and 4) a DustTrak DRX Aerosol Monitor (Model 8534, TSI Inc.) for size segregated mass concentrations (PM_1, $PM_{2.5}$, PM_4, PM_{10}, and PM_{15}) [34].

Real-time instruments generated data every 1–6 s, while integrated samples for laboratory analysis were collected for 20–60 min. Depending on particle concentration and desired collection time, the dilution ratio can be adjusted from one to several thousand. All real-time instruments were deployed for the BioMax®15 experiment, while only the CO_2 analyzers, DustTrak, and CPC operated during the PRFC IBR experiment.

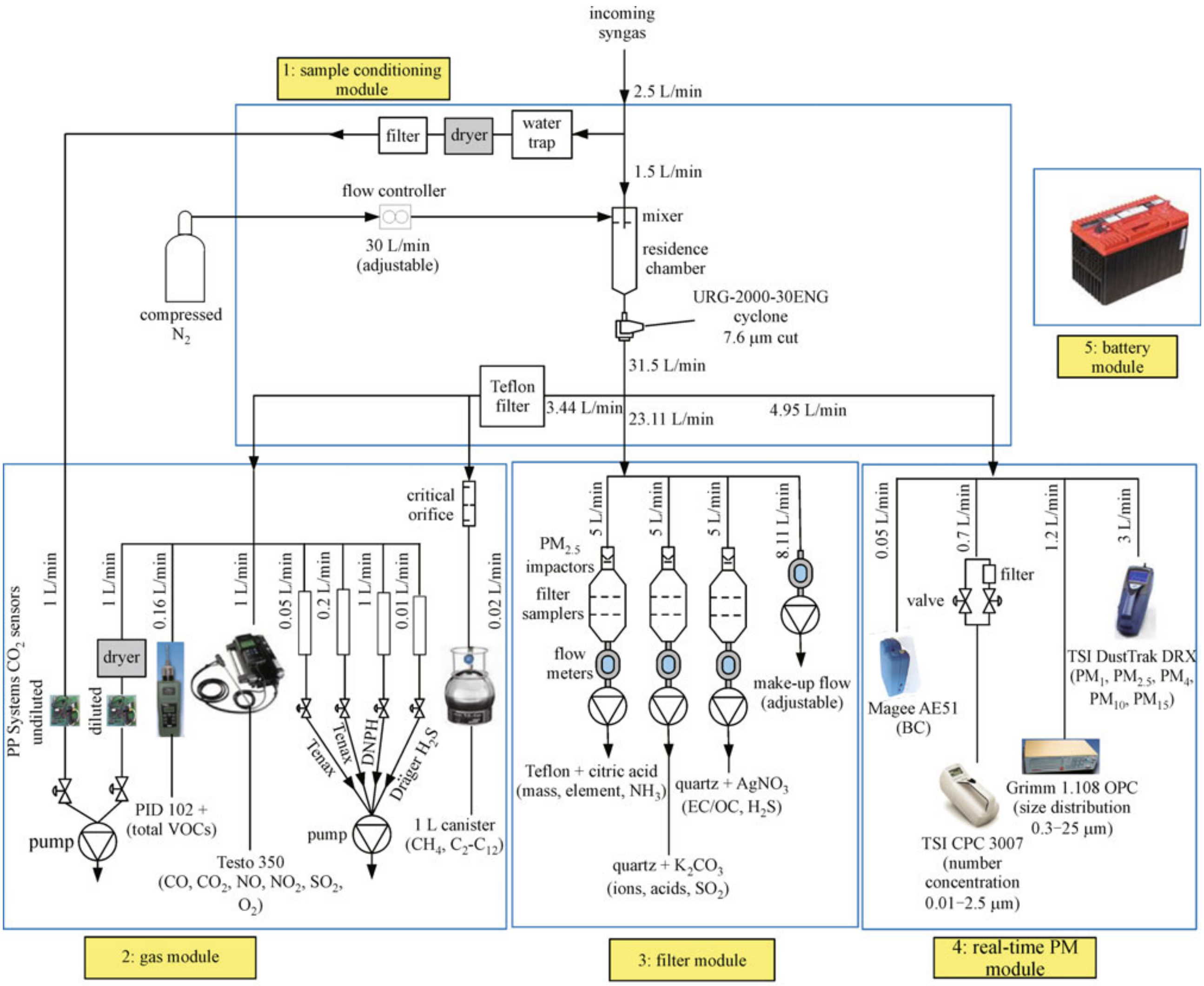


Fig. 2 Schematic of portable dilution sampling system used for syngas characterization

3 Results and discussion

Mass concentration and chemical composition of $PM_{2.5}$ particles collected on filter samples from syngas produced under five different conditions are summarized in Table 1. The average dilution ratio ranged from 1.0 to 13.2, and the listed concentrations were adjusted for dilution. $PM_{2.5}$ mass concentrations in syngas from the BioMax®15 (2247–4835 $\mu g \cdot m^{-3}$) were 2–3 orders of magnitude higher than those from the PRFC IBR downstream of the syngas polisher (12.8–13.7 $\mu g \cdot m^{-3}$) and one order magnitude higher than upstream of this polisher (117.3 $\mu g \cdot m^{-3}$). This is expected since the BioMax®15 combusts syngas to generate electricity and only uses the knockout pot and a fabric filter to reduce particle levels. On the other hand, the PRFC IBR employs an extensive cleaning process to protect the downstream catalyst that converts syngas to transportation fuel. The 12.8–13.7 $\mu g \cdot m^{-3}$ $PM_{2.5}$ concentrations downstream of the PRFC IBR syngas polisher were much lower than the recommended maximum $PM_{2.5}$ level of 500 $\mu g \cdot m^{-3}$ for efficient diesel fuel production using Fisher-Tropsch type catalysts [15,35].

OC, the major portion of tar, was the largest of $PM_{2.5}$ component for all tests. However, OC measured from quartz-fiber filters exceeded the $PM_{2.5}$ concentration measured from Teflon-membrane filters for most cases. This is likely due to positive sampling artifacts caused by organic vapor absorption on the quartz fibers [36,37]. EC in syngas produced from blended wood by the BioMax®15 or from rice hulls in the PRFC IBR contributed to lower than 1% of $PM_{2.5}$, while it was 13%–55% of $PM_{2.5}$ for other test conditions.

Water-soluble ions were lower than 1% of $PM_{2.5}$ mass in syngas from the BioMax®15, but were 16%–27% of $PM_{2.5}$ in syngas from the IBR. The most abundant anions were NO_3^- (0.6–9 $\mu g \cdot m^{-3}$) and SO_4^{2-} (0.4–17 $\mu g \cdot m^{-3}$), while the most abundant cation was NH_4^+ (1.0–15 $\mu g \cdot m^{-3}$). The most abundant elements were Na (1.6–117 $\mu g \cdot m^{-3}$), Mg

Table 1 Comparison of PM$_{2.5}$ mass and chemical constituent concentrations (in $\mu g\cdot m^{-3}$) under different dilution ratios for syngas from BioMax®15 and PRFC IBR. Cells with "<" indicate the species were below the instrument detection limit. Concentrations were normalized to standard temperature (0°C) and pressure (101.3 kPa) conditions

analytical method (filter media)	elements	BioMax®15		PRFC IBR		
		raw wood	blended wood	rice hulls (downstream polisher)	woodchips (downstream polisher)	woodchips (upstream polisher)
CO$_2$ ratios	dilution ratio	13.2	7.1	1.0	1.0	5.0
gravimetry (Teflon-membrane filters)	PM$_{2.5}$ mass concentration	4835	2247	13.72	12.80	117.25
thermal/optical (quartz-fiber filters)	organic carbon (OC)	3949	1151	19.85	23.37	357.28
	elemental carbon (EC)	1220	< 48.48	0.13	1.69	64.72
	total carbon (TC)	5169	1151	19.98	25.06	421.99
ion chromatography (quartz-fiber filters)	chloride (Cl$^-$)	< 90.38	< 41.80	< 0.56	< 0.51	0.59
	nitrate (NO$_3^-$)	8.91	7.75	0.94	0.59	5.21
	sulfate (SO$_4^{2-}$)	17.06	3.06	0.43	0.38	4.77
	ammonium (NH$_4^+$)	14.79	7.45	1.00	0.97	12.86
	sodium (Na$^+$)	< 44.71	< 22.51	0.58	< 0.03	< 0.38
	potassium (K$^+$)	3.12	< 22.73	0.72	0.13	5.74
X-ray fluorescence (Teflon-membrane filters)	sodium (Na)	116.60	3.65	1.56	2.10	24.68
	magnesium (Mg)	47.61	16.06	0.10	0.36	< 2.09
	aluminum (Al)	6.86	1.68	0.94	0.19	7.25
	silicon (Si)	3.49	< 3.99	0.13	0.02	0.17
	sulfur (S)	< 2.15	< 1.08	< 0.09	< 0.06	1.23
	chlorine (Cl)	15.86	0.11	0.40	0.08	1.13
	potassium (K)	16.13	< 1.51	0.47	0.05	0.03
	calcium (Ca)	22.12	0.79	0.04	0.06	< 2.50
	scandium (Sc)	< 39.86	9.64	0.45	0.27	0.43
	titanium (Ti)	5.36	2.32	< 0.05	0.06	< 0.64
	iron (Fe)	11.68	0.48	0.01	0.09	0.09
	zinc (Zn)	< 2.15	< 1.08	0.01	0.08	6.68
	bromine (Br)	0.65	< 1.08	< 0.04	0.03	< 0.52
	lead (Pb)	6.28	1.43	< 0.06	0.01	0.09
	sum of other elements	22.47	16.12	1.31	1.94	23.43

(0–48 $\mu g\cdot m^{-3}$), Al (0.2–7 $\mu g\cdot m^{-3}$), Cl (0.1–16 $\mu g\cdot m^{-3}$), K (0–16 $\mu g\cdot m^{-3}$), and Ca (0–22 $\mu g\cdot m^{-3}$).

Table 1 shows that blending torrefied wood with raw wood yielded PM$_{2.5}$ concentrations 50% lower than those for raw wood alone in the BioMax®15 syngas. Some of the tar-generating components were probably removed during the mild pyrolysis process of torrefaction. The torrefied wood had ~21% higher energy density and resulted in higher gasification temperatures, which might have reduced particle concentrations. No significant differences in PM$_{2.5}$ concentration and composition were observed in the PRFC IBR syngas produced from rice hulls or woodchips. The PRFC syngas polisher efficiently removed ~90% PM$_{2.5}$ mass as is evident from concentrations measured upstream and downstream of this polisher.

Real-time data for gas and PM concentrations in the BioMax®15 syngas are shown in Fig. 3. Average concentrations for the entire run are listed in Table 2 along with other runs. Similar to the observation in filter measurement, the blended wood produced significantly less gases and particulate contaminants.

Examples of particle size distributions measured by the OPC during the BioMax®15 experiments are plotted in Fig. 4. When the feedstock was raw wood, the size distribution was relatively stable and most particles were lower than 1 µm as shown in Fig. 4(a). The average count median diameter (CMD) and mass median diameter (MMD) were lower than 0.3 and 0.51 µm, respectively. Large variations in size distribution were found with

Table 2 Summary of real-time gas and particle concentrations, gravimetric PM$_{2.5}$ mass concentration, particle count median diameter (CMD) and mass median diameter (MMD). Concentrations were normalized to standard temperature (0°C) and pressure (101.3 kPa) conditions

instrument	parameter	BioMax®15		PRFC IBR		
		raw wood	blended wood	rice hulls post-polisher	woodchips post-polisher	woodchips pre-polisher
CO$_2$ analyzer a)	CO$_2$/ppm	5.40E + 04	2.26E + 04	2.43E + 05	2.26E + 05	2.22E + 05
emission analyzer b)	NO/ppm	128.9	32.3	NA h)	NA h)	NA h)
	NO$_2$/ppm	49.8	0.4	NA h)	NA h)	NA h)
	NO$_x$/ppm	178.7	32.7	NA h)	NA h)	NA h)
	O$_2$/ppm	2.6	1.3	NA h)	NA h)	NA h)
PID analyzer c)	VOC/ppm	1689	803	NA h)	NA h)	NA h)
aethalometer d)	BC/(mg·m^{-3})	1.5	0.18	NA h)	NA h)	NA h)
CPC e)	number-CPC (0.01–2.5 μm, cm^{-3})	2.66E + 06	8.21E + 04	9.21E + 03	6.79E + 03	5.63E + 05
OPC f)	number-OPC (0.3–25 μm, cm^{-3})	1.03E + 05	1.41E + 04	NA h)	NA h)	NA h)
DustTrak g)	PM$_{2.5}$-DustTrak/ (mg·m^{-3})	59.2	15.4	0.11	0.02	0.81
OPC	PM$_{2.5}$-OPC/ (mg·m^{-3})	2.4	4.2	NA h)	NA h)	NA h)
teflon filter-gravimetry	PM$_{2.5}$-Gravimetry/ (mg·m^{-3})	4.84	2.25	0.01	0.01	0.12
OPC + CPC	CMD/μm	< 0.3	0.51	NA h)	NA h)	NA h)
OPC + CPC	MMD/μm	< 0.3	1.1	NA h)	NA h)	NA h)

Notes: a) CO$_2$ analyzer: Model SBA-4, PP Systems, Amesbury, MA,USA; b) emission analyzer: Model 350 S, Testo Inc., Sparta, NJ, USA; c) Photoionization detection (PID) analyzer: Model 102 + , PID Analyzers, LLC, Pembroke, MA,USA; d) aethalometer: Model AE51, Magee Scientific, Berkeley, CA, USA; e) condensation particle counter (CPC): Model 3007, TSI Inc., Shoreview, MN, USA; f) optical particle counter (OPC): Model 1.108, Grimm Aerosol Technik GmbH & Co., KG, Ainring, Germany; g) DustTrak: Model 8534, TSI Inc., Shoreview, MN, USA; h) data not available

blended wood feedstock (Fig. 4(b)), with similar CMD (< 0.3 μm) but twofold larger MMD (1.1 μm). The BioMax®15 was designed to operate with raw woodchips. Feedstock blended with torrefied wood generated much more heat and caused less stable gasification, which could in turn have led to larger particle sizes and variable size distributions.

Figure 5 illustrates real-time particle measurements during the BioMax®15 sampling with raw wood feedstock. Figure 5(a) shows that particle number concentrations by OPC (size range ~0.3–25 μm) were reasonably correlated (R^2 = 0.72) with those measured by the CPC (size range ~0.01–2.5 μm). However, the concentration levels measured by the OPC were only ~4% of those by CPC as indicated by the regression slope and the average number concentration shown in Table 2, indicating that ~96% particles were lower than 0.3 μm. For the case with blended wood, the CPC/OPC correlation was lower (R^2 = 0.29, not shown) due to the large variations in size distributions. The OPC concentration increased to 17% of the CPC concentration, consistent with a shift toward larger particles shown in Fig. 4.

The correlation (R^2 = 0.94) between PM$_{2.5}$ mass by the DustTrak and OPC in Fig. 5(b) is expected since both instruments are based on light scattering. However, the slope of linear regression was 13.1, indicating a difference in calibration coefficients relating light scattering to mass. Table 2 also shows that the average PM$_{2.5}$ mass concentrations measured by the DustTrak and OPC during the raw wood run were 59.2 and 2.4 mg·m^{-3}, respectively. The gravimetric PM$_{2.5}$ mass concentration (4.8 mg·m^{-3}) is used to derive conversion factors of 0.082 and 2.02 for the DustTrak and OPC, respectively. Since mass estimates by optical instruments change with particle size and composition [38], the ratio of PM$_{2.5}$ by DustTrak to OPC was 3.7 when running the BioMax®15 with the blended wood feedstock, and the scaling factors to gravimetric mass changed to 0.15 and 0.54 for DustTrak and OPC, respectively. This experiment demonstrates that the optical instruments are useful in providing high-time resolution estimates of mass concentrations. However, their accuracy changes with particle size distribution and chemical composition, and comparisons with gravimetric mass are needed to provide reasonable estimates of mass concentrations. Figures 5(c) and (d) show that the DustTrak PM$_{2.5}$ concentrations were correlated with particle numbers and BC concentrations, with R^2 of 0.81 and 0.71, respectively. Particle number and PM$_{2.5}$ concentrations were also correlated with CO$_2$ (R^2 = 0.75–0.76) as shown in Figs. 5(e) and (f). On the other hand, total VOCs and

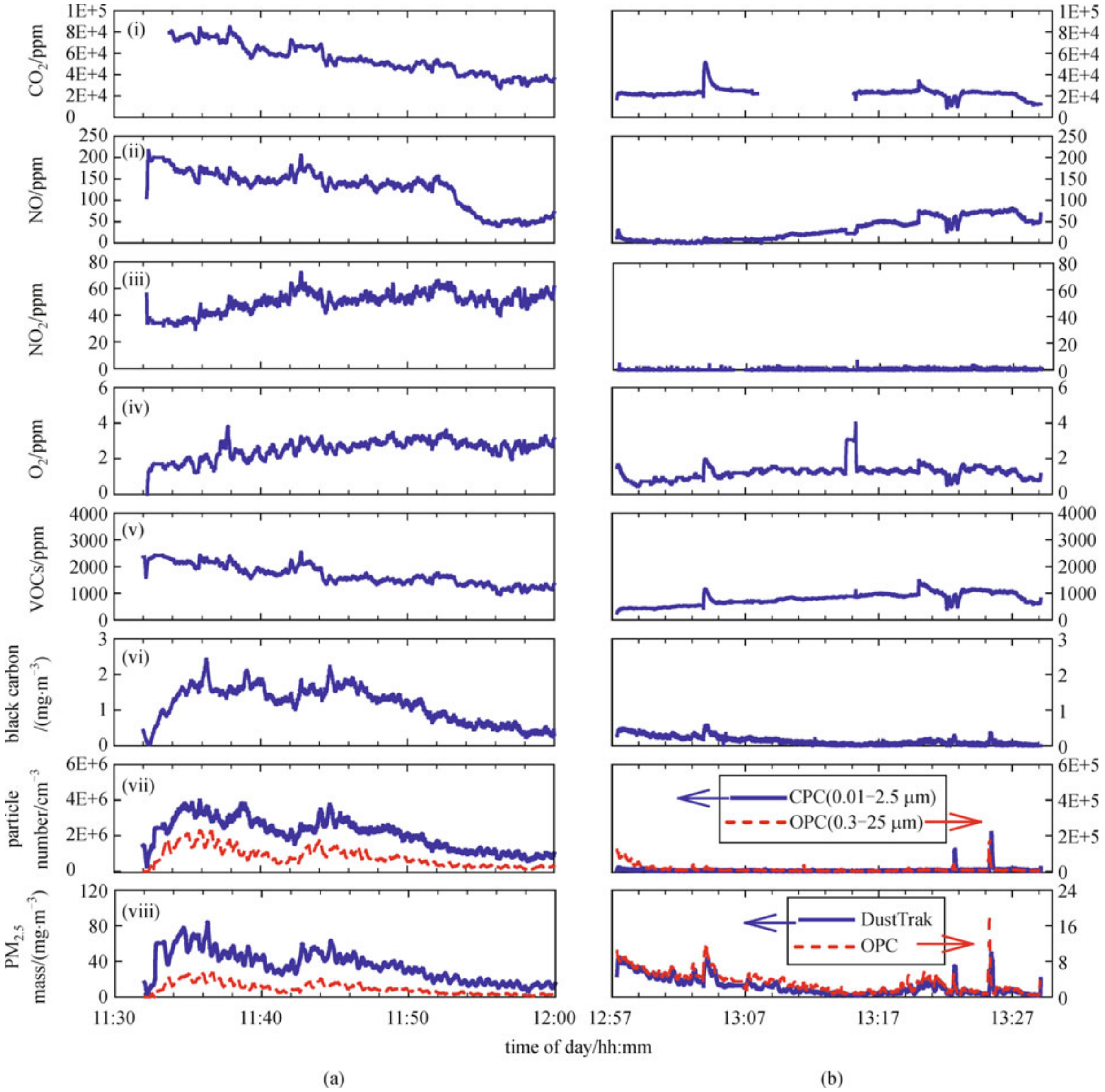
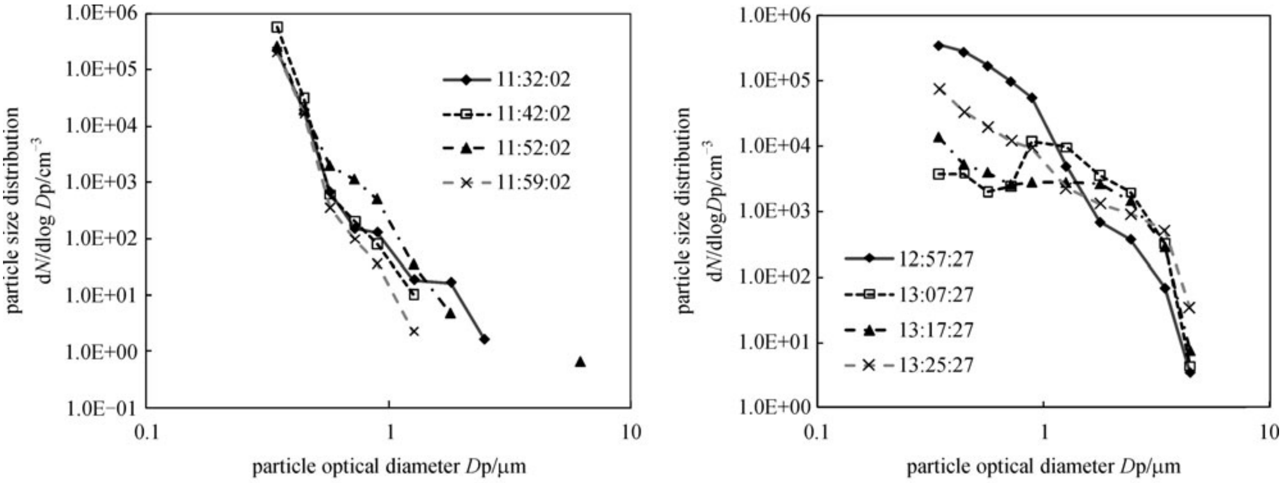


Fig. 3 Time series of (i) CO_2 concentration by CO_2 analyzer; (ii) NO, (iii) NO_2, and (iv) O_2 by emission analyzer; (v) total VOCs by PID analyzer; (vi) black carbon by micro-aethalometer, (vii) particle number concentration by CPC and OPC, and (viii) $PM_{2.5}$ mass concentration measured by DustTrak and OPC in syngas generated from BioMax®15 when the feedstocks were (a) raw wood (left panels) and (b) blended 50% raw and 50% torrefied wood (right panels)

NO_x had poor correlations with particle number and $PM_{2.5}$ ($R^2 < 0.65$, not shown).

Figure 6 compares time series of particle number concentrations measured from syngas produced under different conditions. Also plotted are the particle concentrations measured from diesel engine exhaust and in an air-conditioned office. Diesel exhaust contained the highest particle number concentration (1×10^7 cm^{-3}). Particles in syngas from the BioMax®15 with raw wood feedstock (3×10^6 cm^{-3}) and from upstream of the PRFC IBR syngas polisher (6×10^5 cm^{-3}) were of the same order of magnitude. Particle number concentrations in syngas from the BioMax®15 with blended wood feedstock (8×10^4 cm^{-3}) were 3% of those for the raw wood feedstock (3×10^6 cm^{-3}). Syngas from the IBR downstream of the PRFC syngas polisher (7×10^3–9×10^3 cm^{-3}) had similar concentrations to indoor office air (8×10^3 cm^{-3}).

Due to the low particle levels in syngas generated from the PRFC IBR, $PM_{2.5}$ filter deposits were low, even with no dilution. Longer sample durations (2–4 h) would have acquired a heavier deposit for more precise quantification. However, the high sensitivity of real-time instruments allows in situ quantification of low-level contaminants in the range of 1 μg·m^{-3}, while the dilution mechanism



(a) (b)

Fig. 4 Particle size distribution measured by the optical particle counter (OPC) over the course of syngas sampling from gasification of (a) raw wood and (b) blended wood in the BioMax®15

allowed measurement of higher concentrations in the range of 1 g·m^{-3}. The dilution sampling system is more suitable for measurement of syngas from cleaner processes than the European protocol using filters and impingers which focuses on much higher tar and particle concentration ranges of 1 mg·m^{-3}–300 g·m^{-3} [11,12].

4 Conclusions

A dilution sampling system was deployed to measure gas and particulate contaminants in syngas from two different process plants using multiple biomass feedstocks. The BioMax®15 unit used raw wood and a 50%/50% blended raw and torrefied wood as feedstocks and the syngas was sampled under a reduced pressure (−2.5 kPa), while the PRFC IBR used rice hulls and woodchips as feedstocks and the syngas was sampled at an elevated pressure (70 kPa).

For the integrated samples, a variety of sampling media (canisters, adsorbents, and filters) were employed to collect gas and particle species, followed by off-line laboratory analyses for chemical composition. In addition to $PM_{2.5}$ mass, carbonaceous fractions, water-soluble ions, and elements were acquired. Real-time instruments were utilized to provide measurements of BC, fine particle numbers, and mass concentrations, as well as particle size distributions.

The $PM_{2.5}$ mass concentrations in syngas measured downstream of a syngas polisher in the PRFC IBR using rice hull (13.7 μg·m^{-3}) and woodchip (12.8 μg·m^{-3}) feedstocks were similar, and were lower than the maximum allowable level ($<$ 500 μg·m^{-3}) recommended for catalyst protection. The $PM_{2.5}$ mass concentrations upstream of the PRFC syngas polisher were about one order of magnitude higher (117 μg·m^{-3}) than those of downstream, but still at ~20% of the maximum allowable limit. Therefore, the syngas cleaning process in the PRFC IBR was very efficient. In contrast, the BioMax®15 does not employ rigorous cleaning devices, and the $PM_{2.5}$ mass concentrations (2247–4835 μg·m^{-3}) were 2–3 orders of magnitude higher than those from the PRFC IBR. Blending 50% torrefied wood to raw wood reduced gaseous and particulate contaminants in the BioMax®15 syngas by over 50%. The most abundant chemical constituent of $PM_{2.5}$ was OC. EC was lower than 1% of $PM_{2.5}$ in syngas produced from blended wood in the BioMax®15 or from rice hulls in the PRFC IBR, but was 13%–55% of $PM_{2.5}$ for other test conditions.

The size distribution of particles in syngas generated by the BioMax®15 using raw wood was stable, with most particles less than 1 μm and ~96% particles lower than 0.3 μm (CMD $<$ 0.3 μm and MMD = 0.51 μm). On the other hand, the size distribution of particles generated from blended wood gasification was variable, and particles were significantly larger with ~83% particles lower than 0.3 μm (CMD $<$ 0.3 μm and MMD = 1.1 μm).

Good correlations ($R^2 > 0.9$) were found between $PM_{2.5}$ mass measured by the DustTrak and OPC. However, the ratio of these two instruments, as well as their ratios to gravimetric $PM_{2.5}$ mass concentrations, varied significantly with particle size and composition. Calibration with gravimetric mass is needed to scale these surrogate readings.

Application of dilution sampling is important in enabling reliable characterization of "dirty" syngas. The flexibility of applying different dilution ratios and the high sensitivity of real-time instruments allows measurements to be carried out over a wide dynamic concentration range (from ~1 μg·m^{-3} to 1 g·m^{-3}). Compared to the "standard"

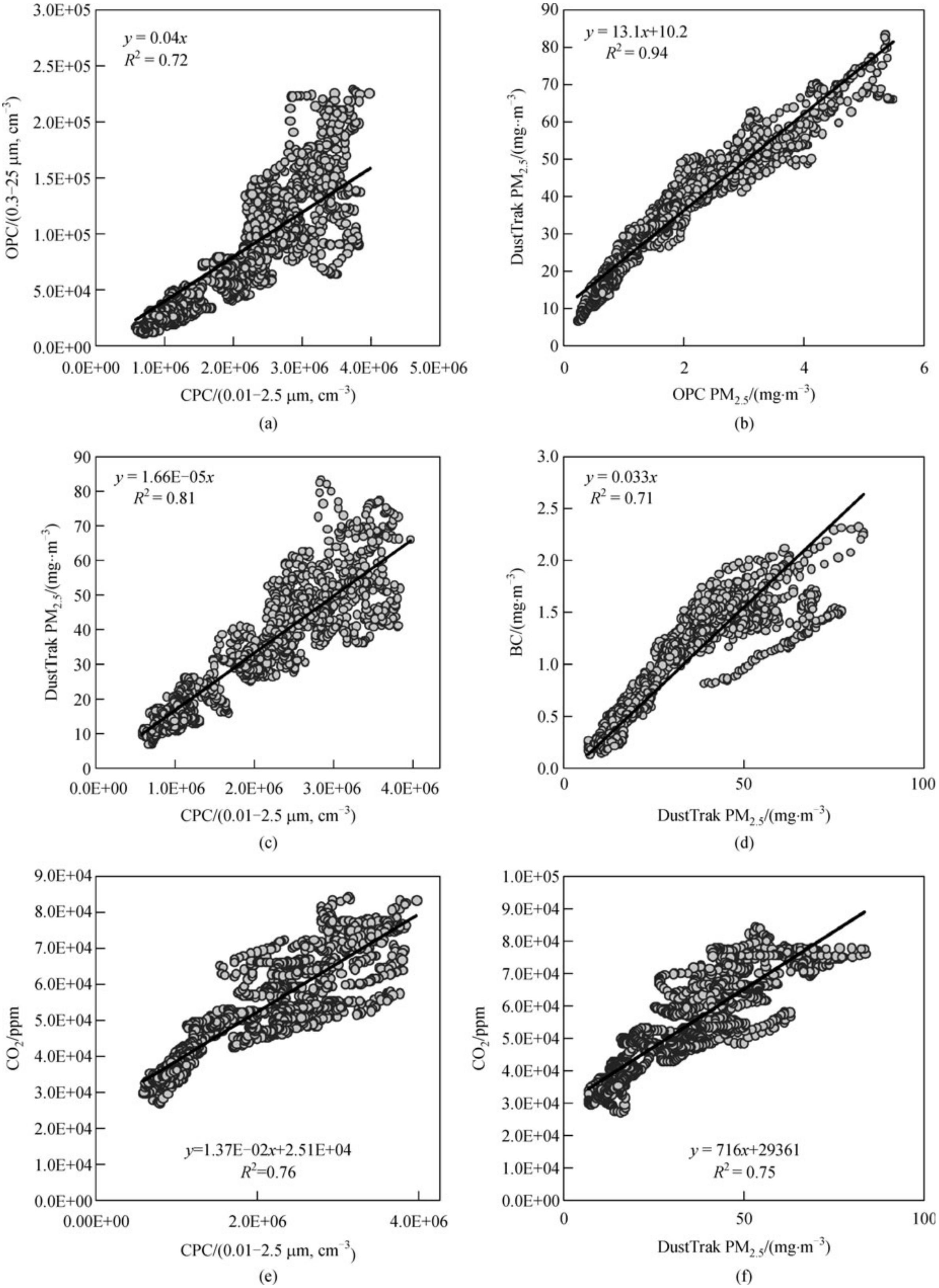


Fig. 5 Relationship between (a) OPC *vs*. CPC for particle number concentration; (b) DustTrak *vs*. OPC for $PM_{2.5}$; (c) DustTrak $PM_{2.5}$ *vs*. CPC number concentration; (d) BC *vs*. DustTrak $PM_{2.5}$; (e) CO_2 *vs*. CPC number concentration; and (f) CO_2 *vs*. DustTrak $PM_{2.5}$ for the BioMax$^{®}$15 run with raw wood feedstock

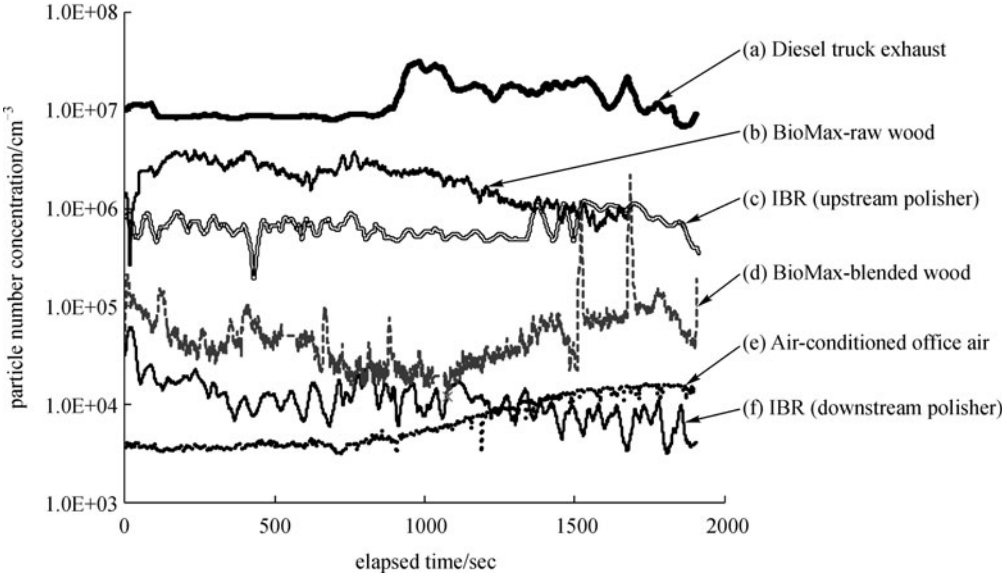


Fig. 6 Comparison of particle number concentrations measured by the CPC from different environments: (a) exhaust from an off-road heavy-duty diesel truck; (b) syngas from BioMax®15 with raw wood feedstock; (c) syngas from the PRFC IBR with woodchip feedstock upstream of the syngas polisher; (d) syngas from BioMax®15 with blended wood feedstock; (e) an air-conditioned office; and (f) syngas from the PRFC IBR with woodchip feedstock downstream of the syngas polisher

filter/impinger syngas sampling protocol, the dilution sampling method is easier to operate, provides data in real-time while collecting integrated samples, and is especially useful for lower concentration range measurements.

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